

First evaluation of iron and manganese concentrations in coastal aquaculture water in Giao Thuy district, Nam Dinh province

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Abstract

Aquaculture in the coastal zone has contributed significantly to economic development in Giao Thuy district, Nam Dinh province. Therefore, water quality for aquaculture plays a vital role in sustainable aquaculture production. In this paper, iron (Fe) and manganese (Mn) concentrations in aquaculture coastal water of Giao Thuy district were analyzed during the rainy season (September 2017, August 2018) and dry season at low tide. The results showed that Fe concentration varied from 0.09 mg/L (at VT5) to 2.42 mg/L (at VT4), averaging 1.12 ± 0.71 mg/L, which exceeded the critical value of the national technical regulation on marine water quality in Vietnam for coastal aquaculture water (QCVN 10:2015/BTNMT) from 1.5 times (at VT4) to 3.0 times (at VT1). Mn concentrations ranged from 0.02 mg/L (at VT9) to 0.10 mg/L (at VT1), averaging 0.05 ± 0.02 mg/L, which was lower than the critical value in the QCVN 10:2015/BTNMT. The results showed that no apparent seasonal variation was observed for both Fe and Mn concentrations. In the dry season, the Fe and Mn concentrations averaged 1.10 mg/L and 0.05 mg/L respectively, whereas they were 1.15 mg/L and 0.05 mg/L in the rainy season. The monitoring results showed that Fe was polluted in the study area and may affect aquaculture productivity. Therefore, helpful measures should be taken to minimize Fe pollution to protect water quality and develop sustainable aquaculture in Giao Thuy district, Nam Dinh province.

Keywords: Iron concentration, manganese concentration, coastal zone, aquaculture, Giao Thuy district.

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INTRODUCTION

As known, metal pollution in many coastal areas of the world has been concerned due to their toxicity and long-term existence that threatens the life of aquatic species and then human health. Within different metals, Fe and Mn are essential to water quality variables in aquaculture because they are required in small quantities by both aquatic plants and animals. However the chemical reactions in sediment and water can have negative impacts on marine life [1]. Fe is an essential nutrient for many organisms, especially for humans. Fe accumulation in seafood may have different effects on human health. Fe deficiency can lead to anemia and impaired intellectual development; however, higher Fe concentrations (e.g. 60 mg/kg for one serving) can cause multi-organ failure, coma, seizures, and even death [2, 3].

Similarly, Mn is an essential element as an antioxidant for blood sugar regulation and bone growth [4]; however, high Mn contents can affect human health, causing a Parkinson-like syndrome, permanent neurological damage, and even death [5]. Noted that the accumulation of metals in aquatic species due to the polluted environmental water was revealed [6, 7]. Thus, the observation of metals concentration in the water environment, especially for water use for aquaculture activities, is vital for ensuring sustainable development of aquaculture.

Previous studies revealed that some metals concentrations in the coastal zone of the Red river, including the coast of Nam Dinh and Thai Binh provinces, were higher than the critical values for coastal water quality QCVN 10-MT:2015/BTNMT. For example, at the Ba Lat estuary of the Red river, at some monitoring time, Mn concentrations in the surface water were from 1.1 times to 2.7 times higher than the allowed value QCVN 10-MT:2015/BTNMT.

Giao Thuy (surface area: 232 km², population: 190,921 inhabitants in 2016) is one coastal district of the Nam Dinh province. Giao Thuy has a coastline of 32 km long, with a flat topography that covers sandy beaches, dunes which are very favorable for aquacultural

development. The surface area for aquaculture in this district is 5,125 ha, with the average value of the total seafood production of 15,000–20,000 tons/year. The main cultured species are clam, shrimp and fish. Aquaculture has contributed proportion significantly to the provincial economy. Seafood processing (about 40 enterprises) has also been developed in recent years. In parallel with aquaculture activities, agriculture, including breeding farms (more than 200 farms) and cultivated land (16,599 ha, of which paddy land is 7,491 ha and vegetable land is 1,500 ha), has played an important role in economic development. The Giao Thuy coastal zone is limited by two river mouths: the Ba Lat mouth of the Red river and the Ha Lan mouth of the So river. In this region, the rainy season lasts from May to October whereas the dry season is from November to April.

However, like many coastal districts, Giao Thuy has suffered from water pollution problems parallel with economic development. Almost all wastewater is untreated and discharged to canals which then flow into the coastal zone and may affect coastal water quality. Thus, the regular monitoring and evaluation of the coastal water quality are critical, especially for ensuring the sustainable development of the aquaculture industry in this area [8].

The paper presents the Fe and Mn concentrations in coastal water in the aquaculture area in Giao Thuy district, Nam Dinh province, for two years, 2017 and 2018. This study aims at investigating Fe and Mn concentrations in coastal aquaculture of the Giao Thuy district. The results may contribute to construct data set of water quality of the Giao Thuy coastal zone, and then provide a scientific basis for protecting coastal water quality and developing sustainable aquaculture in Giao Thuy district, Nam Dinh province.

METHODOLOGY

Surface water samples in the coastal aquaculture areas were collected at nine sites at different communes along the Giao Thuy district: Giao Thien (VT1), Giao An (VT2), Giao Lac (VT3), Giao Xuan (VT4), Giao Hai

(VT5), Giao Long (VT6), Bach Long (VT7), Giao Phong (VT8) and Quat Lam (VT9) (figure 1). Within nine sites, the sites VT1 and VT2 were nearby the Ba Lat mouth of the Red river, whereas the VT9 was nearby the Quat Lam tourist beach and the Ha Lan mouth of the So river.

All surface water samples were taken in 4 sampling campaigns (in the rainy season: September 2017; August 2018; and in the dry

season: November 2017 and January 2018) at low tide, according to TCVN 5998:1995.

Wastewater samples from different sources in the Giao Thuy district, such as domestic ($n = 4$), fishery processing ($n = 4$), husbandry ($n = 4$), agricultural runoff ($n = 4$), and mixed wastewater (canals) ($n = 8$), were collected during the period 2017–2020.

All water samples were kept in an iced box for transportation to the laboratory.

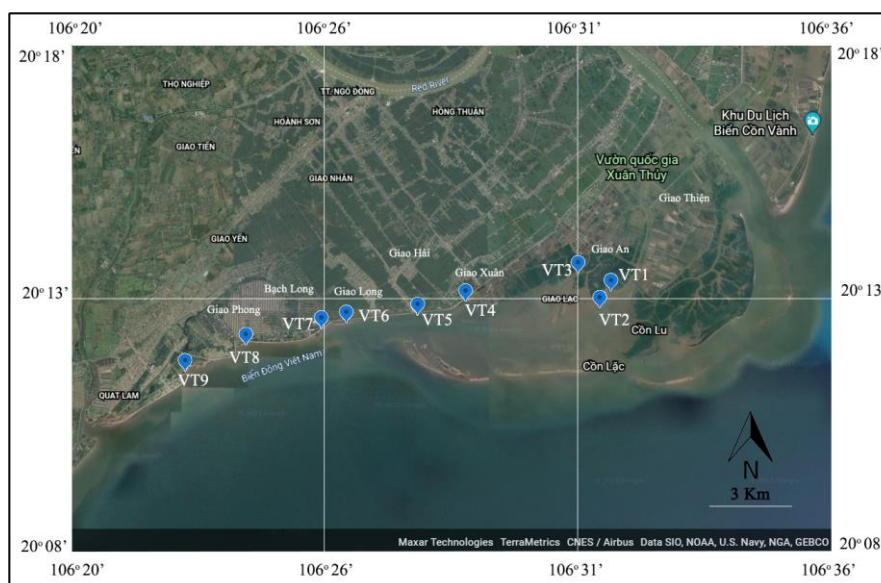


Figure 1. Sampling sites of coastal aquaculture in Giao Thuy district

Total Mn concentration was determined by the method given in the Vietnamese Standard TCVN 6002:1995, and total Fe concentration was analyzed by the method TCVN 6177:1996 on a spectrophotometry UV-VIS V-630 (JASCO, Japan). All analyzes were triplicated, and the final result was the average.

All analytical results were compared to Vietnamese Standards QCVN 10:2015/BTNMT for the coastal seawater quality (applicable to coastal aquaculture) to assess the metal pollution. All statistical and analytical results were performed with t-tests to verify the difference of Fe and Mn values between two seasons (rainy and dry) on the measured mean variables. Probabilities (p) were determined, and a p -value of < 0.05 was considered to be significant.

RESULTS AND DISCUSSION

Spatial variation of Fe and Mn concentrations in coastal Giao Thuy district

The results of Fe and Mn concentrations at nine sites of coastal aquaculture water in the Giao Thuy district during four sampling campaigns in 2017–2018 were presented in table 1.

The results showed that the Fe concentrations in the coastal water samples ranged from 0.09 mg/L to 2.42 mg/L, averaging 1.12 ± 0.71 mg/L for the whole studied region (table 1). Within nine sites, the average value of Fe concentration was lowest at the VT4 site (0.74 mg/L) and highest at VT1 (1.49 mg/L). Fe concentration tended to increase from the site VT4 towards the VT1 site where the Ba Lat mouth of the Red river

discharges directly to the sea. The average value by each site of Fe concentration exceeded from 1.5 times to 3 times than the critical value (0.5 mg/L) of the QCVN 10:2015/BTNMT for the coastal seawater quality (applicable to coastal aquaculture). Noted that increase in Fe concentration in surface seawater can accelerate phytoplankton production and shifts phytoplankton community composition [9] or however precipitation of ferric hydroxide can

coat eggs or cause mechanical obstruction of the gills of fish [1].

Mn concentration in water samples ranged from 0.02 mg/L to 0.10 mg/L, averaging to 0.05 ± 0.02 mg/L for the studied region. This average value was lower than the critical value (0.5 mg/L) of the QCVN 10:2015/BTNMT; however, the mean values of Mn concentration at some sites (VT1, VT7 and VT8) were higher than the critical value (table 1).

Table 1. Fe and Mn concentrations (in mg/L) at 9 sites in coastal aquaculture water of Giao Thuy district, Nam Dinh province in 2017–2018 ($n = 4$)

	Value	VT1	VT2	VT3	VT4	VT5	VT6	VT7	VT8	VT9	QCVN 10:2015/BTNMT
Fe	Average	1.49	1.17	1.02	0.74	1.04	1.10	1.24	1.31	1.00	0.5
	Min	0.21	0.78	0.24	0.16	0.09	0.45	0.74	0.88	0.45	
	Max	2.40	1.86	2.23	2.42	1.56	1.99	2.16	2.24	1.77	
Mn	Average	0.06	0.04	0.03	0.05	0.05	0.04	0.07	0.07	0.04	0.5
	Min	0.03	0.02	0.03	0.02	0.03	0.03	0.04	0.02	0.02	
	Max	0.10	0.08	0.04	0.09	0.08	0.05	0.09	0.09	0.08	

Seasonal variation of Fe and Mn concentration in Giao Thuy coastal district

Our survey results show that at some sites (VT1, VT2, VT3, and VT5), Fe concentrations in coastal aquaculture in the Giao Thuy district tended to be higher in the dry season, but at the remaining sites, they tended to be higher in the

rainy season (table 2, figure 2). Overall, the seasonal difference in Fe concentrations in this study was unclear ($p > 0.05$).

Like Fe, the Mn concentration of aquaculture in coastal areas of the Giao Thuy district showed unclear seasonal variation ($p > 0.05$) (table 2, figure 2).

Table 2. Fe and Mn concentrations in the dry and rainy seasons at nine sites of the coastal aquaculture water in the Giao Thuy district

Sites	Fe (mg/L)		Mn (mg/L)	
	Dry season	Rainy season	Dry season	Rainy season
VT1	2.33	0.64	0.05	0.07
VT2	1.32	1.03	0.04	0.05
VT3	1.44	0.59	0.03	0.03
VT4	0.16	1.32	0.04	0.06
VT5	1.32	0.76	0.04	0.05
VT6	0.75	1.45	0.05	0.04
VT7	1.03	1.45	0.05	0.08
VT8	1.05	1.56	0.08	0.05
VT9	0.50	1.50	0.04	0.05
Average	1.10	1.15	0.05	0.05
Min	0.16	0.09	0.02	0.02
Max	2.40	2.42	0.08	0.10
n	18	18	18	18

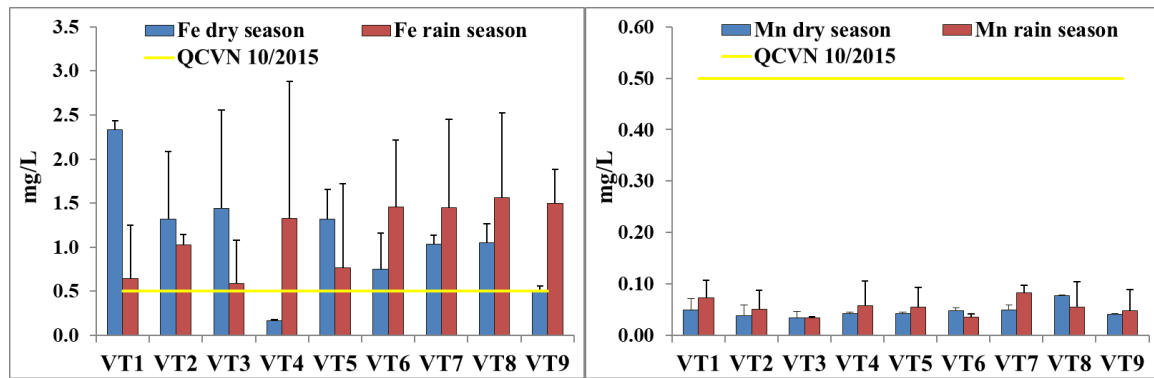


Figure 2. Seasonal variation of Fe and Mn concentrations at 9 monitoring sites in Giao Thuy district, Nam Dinh province in 2017–2018

Comparison with Fe and Mn concentrations in different coastal zones

Fe concentrations have also been observed in some coastal water environments in Vietnam and other coastal zones globally.

In Vietnam, high values of Fe concentration for the coastal zone of Thai Binh province, at Ba Lat estuary were also reported in the previous study that Fe concentrations in 7/25 samples exceeded the critical value of QCVN 10:2015/BTNMT; In other coastal zones in Vietnam, high Fe concentrations were also found in the Bach Dang river estuary (from 1.20 mg/L to 1.65 mg/L, and especially up to 3.6 mg/L in Cua Doi [10] whereas the low values were reported for the Nha Trang bay in the dry season in 2014: 0.05–0.49 mg/L, averaging to 0.23 mg/L [11]) (table 3). A

higher value of Fe concentration in the rainy season (in the range 0.26–0.86 mg/L, mean: 0.56 mg/L) than in the dry season (in the range 0.24–0.75 mg/L, mean: 0.47 mg/L) was noted for the coastal zone of Hai Phong [12].

In the World, Fe concentration reached to very high values of 8.89–18.78 mg/L in the coastal surface water of Giresun (Black sea), Turkey, during the observation period in 2012–2013 [13] or was found in low level, from 0.18 mg/L to 0.35 mg/L in seawater in Australia in 2010 [14] or very low, in the range of 0.01–0.03 mg/L in the Chabarha bay, Oman Sea [15] (table 3). Noted that the Fe concentration regulated by some other countries, e.g., Canada and Russian standards, is lower than the Vietnamese one (0.3 mg/L and 0.1 mg/L respectively) [16].

Table 3. Fe and Mn concentrations in some coastal waters and seawater in the World

No.	Fe concentration, mg/L	Mn concentration, mg/L	Location (year of observation)	References
1	0.01–0.03	0.002–0.009	Chabarha Bay, Oman Sea, Iran (2013)	[15]
2	0.18–0.35	0.007–0.157	South Australian coastline (2010)	[14]
3	8.89–18.78	0.015–0.272	Coastal surface water of Giresun, Turkey (2012–2013)	[13]
4	-	0.063–0.089	Coastal water of Qeshm island, Persian Gulf	[17]
5	0.09–3.38	-	Coastal surface water of Phan Thiet (2008–2009)	[18]
6	0.05–0.49	-	Nha Trang Bay (in 2014)	[11]
7	-	0.002–0.003	Con Dao seawater, Vietnam	[19]
8	3.6	-	Cua Doi, Quang Ninh, Vietnam	[10]
9	-	0.05–0.27	Thai Binh coastal zone	
10	0.09–2.42	0.02–0.10	Giao Thuy coastal zone	This study

Mn concentrations were lower than the ones observed in the previous study for the Thai Binh coastal zone (range 0.05–0.27 mg/L; average: 0.13 mg/L); however, it was much higher than the ones observed in seawater in Con Dao (0.002–0.003 mg/L) [21] (table 3). In the coastal water or seawater in the World, Mn concentrations varied in a high range. The very low values (0.002–0.009 mg/L) were reported for the seawater of the Chabarha bay, Oman Sea [15], whereas higher values from 0.007 mg/L to 0.157 mg/L in seawater in Australia [14] or from 0.015 mg/L to 0.272 mg/L in coastal surface water of Giresun (Black Sea), Turkey during the observation period in 2012–2013 [13] were presented (table 2). Noted that the Mn concentration regulated by other countries, e.g., the Russian standard (0.01 mg/L), is much lower than the Vietnamese one [16].

Sources of Fe and Mn in coastal aquaculture water of the Giao Thuy district

As known, metals such as Fe and Mn in the water environment come from different sources such as industrial production (wastewater from battery production, painting, textile,...), agricultural cultivation (leaching of chemical fertilizers utilization), domestic waste, mining activity (mineral exploitation), landfills (leachate from landfills), and lithology of the area [20].

Some previous studies revealed that high metals concentrations in seawater cannot readily be attributed to mineral weathering and is more likely an indicator of anthropogenic contamination [21, 22]. Indeed, for the case of Nha Trang bay, low Fe concentration in the study site was impacted by natural sources processes whereas in other cases (e.g., the coastal zone of the Red river, or Bach Dang river or in Giresun coast (Black Sea), Turkey), it was controlled by the human activities. For the case of the coastal zone of Hai Phong, high Fe concentrations over the limited value of QCVN10-MT:2015/BTNMT, especially in the rainy season was caused by different inland waste, impacted by the leaching and weathering process [12]. Thus, it is clear that the Fe concentration was significantly different in seawater in the world, depending on the sites observed, and the influence of inland human

waste sources (especially in the coastal towns/cities), and lithological characteristics.

In the case of the Giao Thuy coastal district, our analytical results on wastewater samples in Giao Thuy districts showed that Fe concentrations in mg/L averaged 0.30 ± 0.10 for agricultural runoff; 0.35 ± 0.08 for fishery processing; 0.39 ± 0.13 for domestic; 0.63 ± 0.34 for husbandry; and 0.77 ± 0.41 for canals (mixes) (table 4). Mn concentrations in mg/L averaged 0.08 ± 0.02 for fishery processing; 0.09 ± 0.01 for agricultural runoff; 0.11 ± 0.04 for canals (mixes); 0.12 ± 0.02 for domestic; and 0.17 ± 0.06 for husbandry (table 4).

Our analytical results on Fe and Mn concentrations in coastal surface water of the Giao Thuy district showed no apparent seasonal variation, e.g., Fe concentration averaged 1.10 mg/L and 1.15 mg/L in dry and rainy seasons, respectively. In contrast, Mn concentrations averaged 0.05 mg/L in both seasons, suggesting the impact of complex sources including both point and diffuse sources on these metal concentrations in the Giao Thuy coastal water. This finding may be in line with previous studies that pointed out that the coastal water and sediment quality of the Thai Binh and Nam Dinh provinces probably was impacted by inland sources (domestic, agricultural and industrial wastewater) [23]. For example, Le et al., (2003) [24] reported that water channels in handicraft villages in Nam Dinh province are loaded with trace metal elements, including Fe, exceeding the limits by up to 50 times. Besides, agricultural cultivation with a high application rate of chemical fertilizers may contribute to metal pollution in coastal water in this region [23]. In addition, previous studies revealed that the Fe concentration was very high in the groundwater, especially in the Holocene aquifer in Nam Dinh province, reaching 6.83 mg/L [20]. Besides, lithology and mechanical erosion also play a considerable role in exporting metal to the hydro system. Indeed, a high value (39,110 ppm) in the Red river delta soil was reported [25]. Note that all untreated wastewater discharges to canals and then flows into the coast, together with high Fe

concentration in groundwater and soils may lead to high Fe concentration in the Giao Thuy coastal zone. Thus, pollution sources need to be managed to ensure fishery and aquacultural

seafood quality and safety and provide better environmental quality for the sustainable development of aquaculture in the Red river coastal zone.

Table 4. Fe and Mn concentrations in different wastewater samples in Giao Thuy district

Wastewater		Fe (mg/L)	Mn (mg/L)
Husbandry (n = 4)	Average	0.63	0.17
	min	0.28	0.11
	max	0.99	0.26
	std	0.34	0.06
Domestic (n = 4)	Average	0.39	0.12
	min	0.26	0.11
	max	0.55	0.15
	std	0.13	0.02
Agricultural runoff (n = 4)	Average	0.30	0.09
	min	0.21	0.08
	max	0.42	0.10
	std	0.10	0.01
Fishery processing (n = 4)	Average	0.35	0.10
	min	0.24	0.08
	max	0.41	0.12
	std	0.08	0.02
Canals (mixes) (n = 8)	Average	0.77	0.11
	min	0.25	0.07
	max	1.38	0.19
	std	0.41	0.04
All samples (n = 24)	Average	0.53	0.12
	min	0.21	0.07
	max	1.38	0.26
	std	0.33	0.04

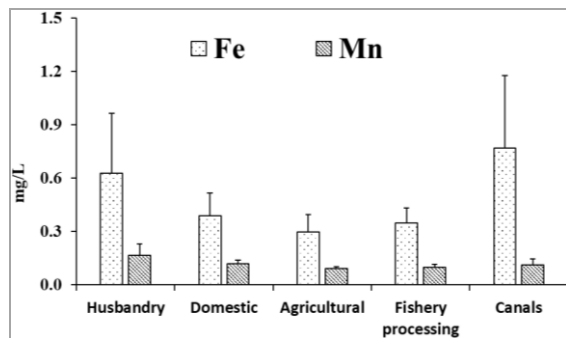


Figure 3. Fe and Mn concentrations in wastewater samples in Giao Thuy district

CONCLUSION

Our survey results of water quality of coastal aquaculture in the Giao Thuy district in 2017–2018 showed that Fe concentration

varied from 0.09 mg/L (VT5, in rainy season) to 2.42 mg/L (VT4, in rainy season), averaging 1.12 ± 0.71 mg/L. The mean Fe concentrations by site exceeded from 1.5 times (VT4) to 3.0 times (VT1) than the critical value of the QCVN 10:2015/BTNMT (applied to surface water quality of coastal aquaculture areas). Mn concentration ranged from 0.02 mg/L (VT9, in rainy season) to 0.1 mg/L (VT1, in the rainy season), averaging to 0.05 ± 0.02 mg/L which were below the critical value of the QCVN 10:2015/BTNMT. The results also revealed that the Fe and Mn concentrations in coastal water did not show an apparent seasonal variation. Indeed, Fe concentration averaged 1.10 mg/L and 1.15 mg/L in dry and rainy seasons, respectively, whereas Mn concentrations averaged 0.05 mg/L in both

seasons. We suggest the impact of complex sources including both point and diffuse sources, on these metal concentrations in the Giao Thuy coastal water.

The monitoring results showed that Fe was polluted in the study area and may affect aquaculture productivity. Therefore, helpful measures should be taken to minimize Fe pollution to protect water quality and develop sustainable aquaculture in Giao Thuy district, Nam Dinh province.

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